PROJECT NUMBER: 6908
PROJECT TITLE: Smoke Condensate Studies
PROJECT LEADER: R. D. Kinser
PERIOD COVERED: February, 1988

I. TSNA PRECURSORS

A. **Objective**: To determine the precursors of MS TSNA.

B. **Results**: Mainstream delivery of nitric oxide on a per cigarette basis was higher for water washed oriental than for the starting material. The possibility that this relates to a nitrosating agent precursor which may be responsible for the increased NNK deliveries seen in other washed fillers will be investigated.

Eight model systems have been selected for consideration for further examination of the role of unextracted nicotine in TSNA pyrosynthesis.

A prototype of a device to measure puff-by-puff nitric oxide in smoke using the TEA as a detector was built and tested. Materials have been ordered to construct a model for routine use in TSNA precursor studies.

C. **Plans**: Evaluate results from nitrate addition and water washing experiments in light of recently acquired nicotine and minor alkaloid information. Determine appropriate model of unextracted nicotine and conduct add-back experiments to evaluate this model as a precursor of MS NNK. Determine the effect on TSNA production of adding NO to the smoke stream at the coal.

D. **References**:

Haut, S. A. Notebook No. 8595, p. 29.
Morgan, W. R. Notebook No. 8579, p. 32.

II. TSNA REMOVAL STUDIES

A. **Objective**: To explore the possibility of extracting TSNA from stored tobacco using an extraction fluid compatible with current processing.

B. **Results**: Experiments were conducted to evaluate the effects of an increased solvent:filler ratio and the effect of a one-hour equilibration time and lower flow rate on the extraction of TSNA and alkaloids from DBC burley with hexane. Analyses of alkaloid and TSNA content of extracted fillers are on-going.

It was determined that cotinine and NNN exhibit similar characteristics under some ion exchange conditions (cation exchange column (SPE); elution with 0.1M phosphate buffer, 10% ammonium hydroxide in 1:1 methanol:water, and 10% ammonium hydroxide in methanol). It appears that cotinine is a suitable model for TSNA

in an evaluation of processes designed to remove alkaloids from an aqueous stream.

C. **Plans**: Continue investigation of cationic exchange SPE cartridges and/or cation exchange resins for TSNA analysis and removal of TSNA and alkaloids. Evaluate the analytical results and determine optimal hexane extraction conditions.

D. **References**:

Warfield, A. H. Notebook No. 8558, p. 61.

III. TSNA ANALYTICAL PROCEDURES

A. **Objective**: To develop and maintain analytical methodology for TSNA determinations which ensures optimal sample throughput, and precision and accuracy of results.

B. **Results**: Experiments were conducted to validate the use of the 20 g alumina column for preparation of samples enriched in VNA as well as TSNA. GC/TEA results indicated no VNA in the TSNA samples and no TSNA in the VNA samples. Quantitative agreement for first analyses was good for the TSNA, and acceptable for the purposes of these analyses for the VNA.

C. **Plans**: Perform replicate smokings and VNA analyses for a reference cigarette.

D. **References**:

Lambert, E. A. Notebook No. 8523, p. 110.

IV. CROSSED SOLUBLES/BASE WEB STUDY (CHEMISTRY)

A. **Objective**: To investigate the smoke chemistry of model cigarettes made from all possible combinations of solubles from bright, burley, and oriental tobaccos on base webs from the same three tobaccos.

B. **Results**: Cigarettes were prepared to investigate the effect of the potassium/calcium ratio on S/M activity and CSC delivery. Salts were dissolved in distilled water and added to Bu CEL, which was then sprayed onto Br base web. Increased calcium (added as calcium acetate) resulted in decreased TPM and significantly reduced sidestream visibility. Control K:Ca ratio was 1.58:1; K:Ca ratios of approximately 1:2 and 1:3 yielded the reduced TPM and sidestream visibility. Increased levels of calcium also resulted in collection of less impaction trapped CSC.

C. **Plans**: Additional experiments have been planned to replicate these results and to include more controls to assist in data interpretation.

D. **References**:

Williams, D. L. Notebook No. 8530, p. 57.

V. OPTIMIZATION OF A LOW ACTIVITY MODEL: MS NITRIC OXIDE CONTENT

A. **Objective**: To develop methods of reducing MS NO delivery for a low activity model.

B. **Results**: Four types of filter treatments designed to reduce mainstream NO delivery have been identified: application of diene generators to the filters, addition of ferrous chelates to the filters, addition of spin traps to filters, and addition of oxidation/adsorption agents to filters. Materials have been ordered to begin evaluation of these methods. The necessary analytical equipment to determine NO deliveries with a nitrate selective electrode are also on order.

C. **Plans**: Validate analytical methodology and begin evaluation of the various filter additives.

D. **References**: Levins, R. J. Notebook No. 8550, p. 87.

VI. SUPPORT FUNCTION: CONDENSATE PREPARATION

A. **Objective**: To fabricate cigarettes, perform smokings, and prepare condensate as needed for biological and chemical analysis.

B. **Results**: Fifty-six smokings of 17 different cigarette codes were conducted to provide condensate for various chemical and biological assays.

Acid, base, and neutral fractions were prepared from condensate from two different codes for Dr. G. Patskan.

D. **References**:

Hellams, R. D. Notebook No. 8613, p. 8.
Lambert, E. A. Notebook No. 8523, p. 110.
Tickle, M. H. Notebook No. 8587, p. 81.